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The Two Electron Oxidation of Cobalt Phthalocyanines by Thionyl Chloride.
Implications for Lithium/Thionyl Chloride Batteries

By

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in

Inorganic Chemistry

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**The Two Electron Oxidation of Cobalt Phthalocyanines by Thionyl Chloride.
Implications for Lithium/Thionyl Chloride Batteries**

P.A. Bernstein and A.B.P. Lever*

Cyclic voltammetry, DPV and electronic spectroscopy are used to study the reaction between thionyl chloride and cobalt phthalocyanine. SOCl_2 reacts with $[\text{Co(I)TnPc(2-)}]^-$ and Co(II)TnPc(2-) to give two-electron oxidized species. Implications for Li/ SOCl_2 batteries are discussed. Thionyl chloride also forms a mono SOCl_2 adduct with Co(II)TnPc(2-) . Driving forces (ΔE values) have been calculated for CoTnPc comproportionation and $\text{CoTnPc} + \text{SOCl}_2$ reactions. Rest potential measurements of a Li/ SOCl_2 cell show that addition of AlCl_3 stabilizes the LiCl product as LiAlCl_4 . A catalytic two-electron mechanism is indicated for the reduction of thionyl chloride in a Li/ SOCl_2 /(CoTnPc,C) battery.

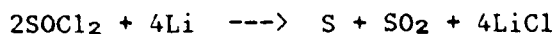
Introduction

The lithium/thionyl chloride (SOCl_2) cell is the highest energy density system known to date.¹ The battery consists of a lithium anode, a

10/4/89

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carbon cathode, an inorganic electrolyte and thionyl chloride which functions both as the solvent and cathode active material. The most generally accepted cell reaction involves the formation of sulphur, sulphur dioxide and lithium chloride.²



Intermediate species such as S_2Cl_2 , SCl_2 , SO , S_2O , SO_2 and SO_2Cl_2 have been reported.^{1,3-8} The use of Li/SOCl_2 batteries has been greatly restricted, however, because of the explosion hazard. Studies⁹ have shown that unstable intermediates from SOCl_2 reduction are responsible for spontaneous exothermic reactions in discharged cells. Safety vents can be installed in Li/SOCl_2 batteries to release excessive pressure and have been successful in preventing explosions.¹⁰⁻¹²

Doping of the carbon cathode with iron or cobalt phthalocyanine complexes improves the cell voltage, the rate of discharge and the lifetime of Li/SOCl_2 batteries.¹³⁻¹⁹ Doddapaneni¹³⁻¹⁶ reports that the electrode kinetics and the cell reaction are different at phthalocyanine-containing cathodes. His rotating disk electrode studies¹⁶ show that 1.36 times more electrons are transferred to each SOCl_2 molecule at an FePc treated carbon electrode than at a bare carbon electrode. For example, if SOCl_2 is reduced for by two electrons at an FePc electrode then 1.47 electrons, on the average, are transferred to each SOCl_2 molecule at a bare carbon electrode. In this current work, the reaction of thionyl chloride with cobalt phthalocyanine was studied to understand the function of phthalocyanines in lithium/thionyl chloride cells.

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Experimental

Cobalt tetraneopentoxypthalocyanine (abbreviated CoTnPc) was used because of its increased solubility in organic solvents and was prepared by the method published by Leznoff and coworkers.²⁰ Nitrogen (dried over drierite) was bubbled through thionyl chloride (reagent grade, BDH) for five hours prior to use to remove all traces of HCl and dissolved oxygen. 1,2-dichlorobenzene (DCB)(Gold Label, Aldrich), an inert solvent, was dried over 4Å molecular sieves (8-12 mesh, Aldrich) activated at 200°C under vacuum for two hours. Tetrabutylammonium hexafluorophosphate (TBAPF₆)(98%, Aldrich) was recrystallized from absolute ethanol and dried at 140°C under vacuum for two hours. Tetrabutylammonium chloride (TBACl) (Eastman) was dried using molecular sieves as an 0.10M solution in DCB.

Electronic spectra were recorded with a Guided Wave Inc. Model 100-20 optical waveguide spectrum analyzer using a caliper fiber optic probe and a 0.100 or 0.200 cm quartz cell. Electrochemical data were obtained with either a Pine Model RDE3 double potentiostat, a Princeton Applied Research (PAR) Model 174A polarographic analyzer coupled to a PAR Model 175 universal programmer, or a PAR Model 173 potentiostat/galvanostat coupled to a PAR Model 179 digital coulometer. The PAR 174A analyzer, set in the differential-pulse mode, was used to perform differential-pulse voltammetry (DPV or DP voltammetry). Cyclic voltammetry (CV) and DPV were carried out under nitrogen using a conventional three-electrode cell. A platinum pseudo-micro disk described by the cross-sectional area of a 27-gauge wire (area $1.02 \times 10^{-3} \text{ cm}^2$) sealed in soft glass or a platinum wire was used as the working electrode. A platinum wire served as the counter electrode, and a silver wire coated with silver chloride was used as a quasi-reference

10/4/89

---4---

electrode. The AgCl/Ag reference was isolated from the main solution by a medium glass frit. Potentials were referenced internally to the ferrocenium/ferrocene (Fc^+/Fc) couple²¹ which occurred at +0.49V vs a platinum-tipped saturated calomel electrode (SCE) in DCB.

The bulk electrolysis cell consisted of a relatively large platinum-mesh working electrode, platinum-wire counter electrode and silver chloride/silver wire quasi-reference electrode. Both the counter and reference electrodes were separated from the working compartment by medium glass frits. All solutions used for electrochemistry contained ca. 10^{-4}M CoTnPc in DCB and 0.1M TBAPF₆ or TBACl as supporting electrolyte, and were deoxygenated by bubbling nitrogen for two hours prior to use.

Li/SOCl₂/C cells were prepared (in air) using a piece of ordinary pyrolytic graphite (OPG) as the cathode and lithium wire as the anode. The lithium was cut under the thionyl chloride solution to expose a fresh surface of metal. Rest potentials were measured using a Fluke 75 digital voltmeter and the potential of each electrode was measured versus a platinum-tipped SCE.

$[\text{Co(I)TnPc(2-)}]^-$ was prepared by bulk electrolysis (-1.00V vs AgCl/Ag, under N₂) of a Co(II)TnPc(2-) solution containing TBAPF₆. $[\text{Co(I)TnPc(2-)}]^-$ was also prepared chemically by reducing a $2.3 \times 10^{-4}\text{M}$ solution of Co(II)TnPc(2-) in DCB containing 0.07M TBAPF₆ using a thin piece of graphite (0.5mm, HB pencil lead) inserted into a piece of lithium. This reaction was performed in a 0.100 cm quartz cell under nitrogen. $[\text{Co(III)TnPc(2-)}]^+$ was prepared by bulk electrolysis (+0.90V vs AgCl/Ag, under N₂) of a Co(II)TnPc(2-) solution containing TBACl.

In a typical experiment, 1 μl of SOCl₂ (1.4×10^{-5} moles, 140X excess) was added to a 1 ml DCB solution of CoTnPc (10^{-4}M) under nitrogen.

10/4/89

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Rigorously dry conditions were used to prevent hydrolysis of SOCl_2 ²² which would lead to protonation of the phthalocyanine by the HCl produced.

Results

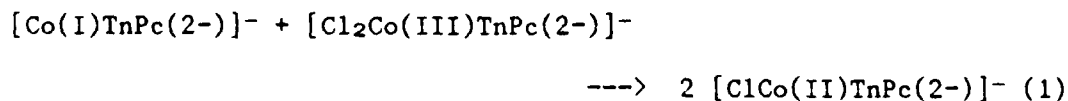
Electronic Spectroscopy.— The oxidation and reduction processes on the cobalt phthalocyanine unit can take place either at the metal or at the organic ligand center.²³ The electronic spectra of cobalt tetraneopentoxypthalocyanine species in the $[\text{Co(I)TnPc(2-)}]^-$, Co(II)TnPc(2-) and $[\text{Co(III)TnPc(2-)}]^+$, as well as the oxidized TnPc(1-) and reduced TnPc(3-) oxidation states have been previously reported.²³⁻²⁵ (Table 1,c,e,j,m) Thus electronic spectroscopy provides a rapid and reliable method for assessing redox level changes occurring during the reactions described here between CoTnPc species and SOCl_2 . The following chemistry is monitored by the electronic spectroscopic changes which occur when thionyl chloride, and other reagents where relevant, were added to a solution of CoTnPc in a specific oxidation state. The electronic spectra are usually sensitive to the nature of the axial groups, if any, attached to the central cobalt ion, and thus such axial groups can often be deduced.

1. Solution reaction of $[\text{Co(I)TnPc(2-)}]^-$ with SOCl_2

When a small excess of thionyl chloride (4 equivalents) was added to an electrochemically generated solution of $[\text{Co(I)TnPc(2-)}]^-$ in DCB the cobalt phthalocyanine was rapidly oxidized (in seconds) by two electrons to $[\text{Co(III)TnPc(2-)}]^+$ (Figure 1, Table 1,h). To within experimental error, the spectrum of the oxidized product is identical to that obtained when Co(II)TnPc(2-) is oxidized electrochemically in DCB/TBACl (Table 1,i). Since

a cobalt(III) centre strongly favours a six coordinate low spin configuration,²⁶ this product must certainly be $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$, the dichloride complex, analogous to the $[(\text{DMF})_2\text{Co(III)TnPc(2-)}]^+$ complex previously characterized.²³ (Table 1,j)

If the thionyl chloride is added to a $[\text{Co(I)TnPc(2-)}]^-$ DCB solution and not mixed, then a blue layer (confirmed to be Co(II)TnPc(2-) by electronic spectroscopy) slowly forms (minutes) between the unreacted $[\text{Co(I)TnPc(2-)}]^-$ (yellow) and the newly created $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ (green). The Co(II)TnPc(2-) results from the reaction,



when the $[\text{Co(I)TnPc(2-)}]^-$ and $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ layers come into contact with each other. This reaction is very favorable (Table 2,(i)).

Equation 1 indicates that the cobalt(II) phthalocyanine species is formed as a chloride adduct and this was confirmed by comparing the spectrum of the Co(II)TnPc(2-) product to that of Co(II)TnPc(2-) in DCB containing TBACl (Table 1,f). Binding of chloride ions to Co(II)TnPc(2-) affects the electronic spectrum by broadening and blue shifting the Q-band, and increasing the intensity of the Soret band at 347 nm (see Figure 2).

2. Solution reaction of Co(II)TnPc(2-) with SOCl_2

The reaction between thionyl chloride and Co(II)TnPc(2-) in DCB proceeds through several stages. There is a small shift and broadening of the Q band in the electronic spectrum immediately after the addition of SOCl_2 (Figure 2, Table 1,g). The spectrum is still typical of a Co(II)

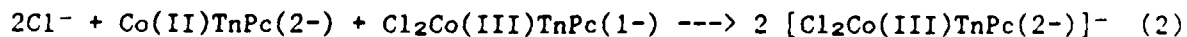
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phthalocyanine species²³ and thus the product is inferred to be the adduct (SOCl₂)Co(II)TnPc(2-).

After the formation of the (SOCl₂)Co(II)TnPc(2-) adduct, two-electron oxidation proceeded cleanly (isosbestic points), within minutes, to form Cl₂Co(III)TnPc(1-) (Figure 3, Table 1,k). Since the starting spectrum of Co(II)TnPc(2-) does not pass through the isosbestic points all of the Co(II)TnPc(2-) was converted to the (SOCl₂)Co(II)TnPc(2-) adduct (perhaps some was directly oxidized to Cl₂Co(III)TnPc(1-)) immediately after the addition of SOCl₂. The identity of the phthalocyanine ring oxidized radical TnPc(1-) species is assured by its electronic spectrum^{24,25} and esr²⁴ while the presence of the two chloride ions is assumed since they will be required by the six coordinate cobalt ion; moreover species of this type have been previously identified.²⁴ Indeed further verification of this species was obtained when chlorine gas was used to generate it instead of thionyl chloride. The electronic spectra of the two [Co(III)TnPc(1-)]²⁺ products (Table 1, k and l) were virtually the same except for a decrease in the extinction coefficients for the chlorine gas case due to slight decomposition of the cobalt phthalocyanine.

The comproportionation reaction,



was also observed in DCB solution using electronic spectroscopy, but only in the presence of additional chloride ions. This indicates the importance of coordinating ligands, chloride in this case, for the production of Co(III)Pc species ($\Delta E = +0.82\text{V}$, reaction (ii) in Table 2).

3. Solution reaction of $[\text{Co(III)TnPc(2-)}]^+$ with SOCl_2

Addition of excess thionyl chloride (40 equivalents) to a solution of $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ in DCB (prepared from the reaction of $[\text{Co(I)TnPc(2-)}]^-$ with a small excess of SOCl_2 (4 equivalents)) subsequently yielded $\text{Cl}_2\text{Co(III)TnPc(1-)}$ as indicated by electronic spectroscopy. The reaction between $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ and SOCl_2 was slow, taking about 30 minutes to go to completion. Thionyl chloride did not oxidize the $\text{Cl}_2\text{Co(III)TnPc(1-)}$ further, even after adding more SOCl_2 (up to 9000 equivalents) and heating at 50°C for thirty minutes. Dissolution of Co(II)TnPc(2-) in neat thionyl chloride also yields $\text{Cl}_2\text{Co(III)TnPc(1-)}$.

[Note, that at low SOCl_2 concentrations $[\text{Co(I)TnPc(2-)}]^-$ can be observed to stop at the $[\text{Co(III)TnPc(2-)}]^+$ stage since oxidation to $\text{Cl}_2\text{Co(III)TnPc(1-)}$ is very slow under such conditions.]

Cyclic Voltammetry and Differential-Pulse Voltammetry.-

1. Cyclic voltammetry of Thionyl Chloride

Thionyl chloride has been the subject of several electrochemical investigations^{1,7,16,17,27,28} which have revealed remarkable complexity. In summary, there is a two-electron reduction of thionyl chloride initially to form "SO" and 2Cl^- with the former reacting further to yield sulphur and SO_2 . The voltammogram of SOCl_2 shows the initial two-electron reduction peak at ca -0.75V (vs AgCl/Ag) in organic solvents together with waves due to the reduction of the S and SO_2 which are generated. SO_2 reduction occurs at ca -0.95V while there are two reduction waves involving sulphur at about -0.7 and -1.5V . There is some variation in these values depending on the solvent used.

In our studies some control experiments were undertaken to evaluate which waves arose from thionyl chloride reduction, and which involved CoTnPc. Blank runs were performed in DCB/TBAPF₆ in which CoTnPc, SOCl₂, S and Cl⁻ were each studied individually. Under these solvent conditions, thionyl chloride exhibits its two-electron reduction peak at -0.69V but with some dependence upon thionyl chloride concentration, as previously observed.¹ We observe sulphur reduction peaks (solution obtained by dissolving elemental sulphur in DCB) at -0.98 and -1.26V and chloride oxidation (1.8 X 10⁻³M solution of TBACl in DCB) at 0.75V vs AgCl/Ag.

The chloride which is generated in the thionyl chloride reduction process is oxidized at 0.77V vs AgCl/Ag, in DCB solution, ca 0.3V less positive than previously noted in other organic solvents.^{1,7} Chloride ion is probably destabilized in DCB, a very nonpolar solvent, making oxidation of chloride to chlorine gas more favorable.

2. Cyclic Voltammetry of CoTnPc/SOCl₂

The cyclic voltammogram of cobalt tetraneopentoxypthalocyanine in DCB, has been previously reported and analyzed.²³ The molecule undergoes quasi-reversible one-electron reductions and oxidations ($i_a = i_c$, $i_{av} \neq i_{cv}$). The first reduction process (I) yields [Co(I)TnPc(2-)]⁻, while the first two oxidation processes, (II) and (III), generate [Co(II)TnPc(1-)]⁺ and [Co(III)TnPc(1-)]²⁺ respectively. To study the effect of thionyl chloride on the CoTnPc waves, microlitre amounts of SOCl₂ (oxygen and HCl free) were added to an electrochemical cell containing Co(II)TnPc(2-) in DCB.

When the thionyl chloride was added to the cell containing Co(II)TnPc(2-) in DCB/TBAPF₆, oxidation of the bulk solution to Cl₂Co(III)TnPc(1-) occurred over a period of about 10 minutes. The cyclic

voltammogram and DPV of CoTnPc in the presence of SOCl_2 is therefore the voltammetry of $\text{Cl}_2\text{Co(III)TnPc(1-)}$ and is shown in Figure 4; the results are listed in Table 3. All of the SOCl_2 and CoTnPc waves were well separated from each other except for the $\text{Co(II)TnPc(2-)/[Co(I)TnPc(2-)]^-}$ wave (I) which was obscured by SOCl_2 reduction in the CV experiment, but was observable using DPV (Figure 4).

Recording the CV or DP voltammogram from +1.5 to +0.3V vs the AgCl/Ag reference electrode eliminated the interference from the Cl^- oxidation reaction, since chloride ions are not produced until SOCl_2 is reduced.

Before the addition of any SOCl_2 , the $[\text{Co(II)TnPc(1-)}]^+/\text{Co(II)TnPc(2-)}$ redox couple (II) appeared as a double wave probably due to aggregation effects. After the addition of SOCl_2 only one such wave was observed in the cyclic and DP voltammograms. Redox couples (I) and (III) in Table 3 shifted negatively in the presence of SOCl_2 . Current ratios (i_a/i_c) for all of the cobalt phthalocyanine couples were equal to unity except for the $\text{Co(II)TnPc(2-)/[Co(I)TnPc(2-)]^-}$ couple (I) which was equal to 0.91 (measured against a pure SOCl_2 background to correct for the SOCl_2 current) when SOCl_2 was present [DPV, scan rate 5mV/s, 1.5X free SOCl_2].

Two sets of data are listed in Table 3 for the electrochemistry of CoTnPc in the presence of different concentrations of SOCl_2 . The Co(II)/Co(I) couple (I) could not be observed in the presence of a significant excess of thionyl chloride but could be studied with a small excess. Also listed in Table 3 are the half-wave potentials of CoTnPc in the presence of chloride ions (TBACl). These will be used later to analyze the redox couples of CoTnPc in the presence of SOCl_2 .

Rest Potential Measurements.— The open circuit rest potentials of various $\text{Li/SOCl}_2/\text{C}$ cells are listed in Table 4. E_a represents the Li^+/Li

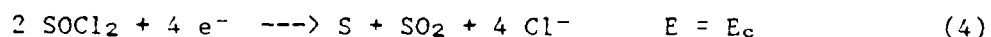
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couple in SOCl_2 vs SCE under the conditions stated in Table 4:



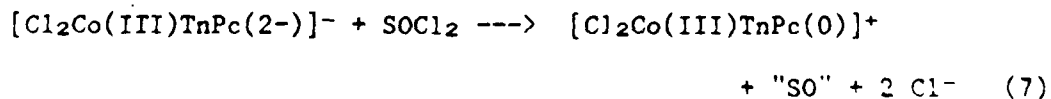
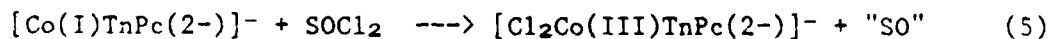
while E_c represents the liquid SOCl_2/C couple vs SCE:



The difference between E_c and E_a should theoretically equal the potential of the cell (E_{cell}) and this was observed within a tenth of a volt.

Discussion

Electronic Spectroscopy.— The following two-electron redox reactions between thionyl chloride and CoTnPc , can be considered.

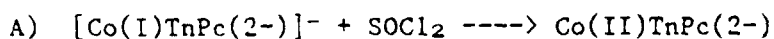


"SO" represents the initial reduction product of SOCl_2 but is likely to react further (see below). Reactions 5 (fast) and 6 (slow) are observed, but 7 is not. Oxidation process 5 involves the two-electron oxidation of

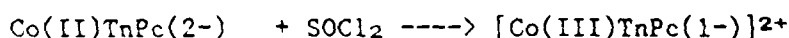
$[\text{Co(I)TnPc(2-)}]^-$ and not two sequential one-electron oxidations via Co(II)TnPc(2-) since the latter is not observed as a one electron oxidation intermediate. Similarly, no intermediate oxidation product is observed when reaction 6 is followed via electronic spectroscopy.

Further evidence that $[\text{Co(I)TnPc(2-)}]^-$ is directly oxidized by two electrons to $[\text{Co(III)TnPc(2-)}]^+$ arises when reactions 5 and 6 are taken together. If, for example, $[\text{Co(I)TnPc(2-)}]^-$ is oxidized by one electron to Co(II)TnPc(2-) then one would observe either A or B below.

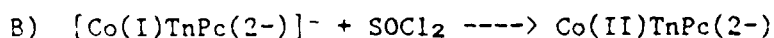
fast



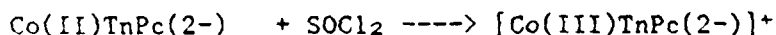
slow



fast

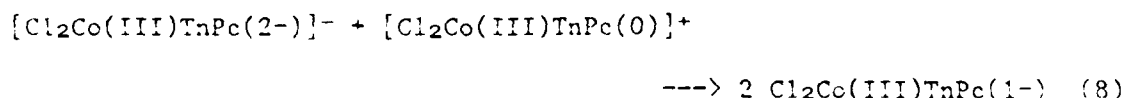


fast



The reaction between $[\text{Co(I)TnPc(2-)}]^-$ and SOCl_2 must be fast because reaction 5 is fast. In case A the Co(II)TnPc(2-) reacts with thionyl chloride to give $\text{Cl}_2\text{Co(III)TnPc(1-)}$ according to reaction 6. This would result in a build up of Co(II)TnPc(2-) and the lack of production of $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$, contrary to reaction 5. Case B, on the other hand, would satisfy reaction 5, but would contradict reaction 6. Hence, $[\text{Co(I)TnPc(2-)}]^-$ must be oxidized directly to $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ by thionyl chloride without stopping at the Co(II)TnPc(2-) stage.

Thionyl chloride oxidizes $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ to the one electron oxidation product $\text{Cl}_2\text{Co(III)TnPc(1-)}$ and not to the two-electron oxidation product $[\text{Cl}_2\text{Co(III)TnPc(0)}]^+$. It is possible that the SOCl_2 could have effected two-electron oxidation but then upon mixing,



There was no electronic spectroscopic evidence, however, for the two-electron oxidation product. Indeed, the potential for the production of $[\text{Co(III)TnPc(0)}]^{3+}$ is very unfavorable.²³ Table 2 lists the driving forces (ΔE values) for many CoTnPc and SOCl_2 reactions. All of the reactions in Table 2 were observed in DCB solution, even reactions (iv) and (v) which have unfavorable ΔE values.

(SOCl₂)CoTnPc Adducts

Addition of thionyl chloride to Co(II)TnPc(2-) in DCB solution first yielded a $(\text{SOCl}_2)\text{Co(II)TnPc(2-)}$ adduct (Figures 2 and 3, Table 1,g). A Co(II)TnPc(2-) mono thionyl chloride complex is proposed for the following reasons:

- The spectrum of the adduct after the addition of one equivalent of SOCl_2 to Co(II)TnPc(2-) was the same as that obtained when a fifty fold molar excess of SOCl_2 was added. This implies that not more than one molecule of SOCl_2 is coordinating to the Co(II)TnPc(2-) .
- The cobalt phthalocyanine was still in the Co(II)Pc(2-) oxidation state as indicated by its electronic spectrum.²³

- Co(II)Pc(2-) favors the formation of five coordinate complexes.²⁹

It is not certain at this time whether the oxygen or sulphur atom of SOCl₂ is coordinating to the Co(II) metal center.

It is also possible that SOCl₂ could coordinate to the phthalocyanine ligand. Brønsted acids, do indeed, protonate phthalocyanines and it is believed that the protons bind to the outer nitrogen atoms of the pc ring.³⁰⁻³³ When the phthalocyanine is protonated the Q band in the electronic spectrum shifts (ca 30 nm per bound proton) to longer wavelengths. Since shifts of this kind were not observed in the reactions with SOCl₂, interactions between thionyl chloride (acting as a Lewis acid) and the phthalocyanine ring were minimal.

Cyclic Voltammetry and DPV of CoTnPc.- The electrochemistry of CoTnPc in the presence of thionyl chloride was complicated by the SOCl₂ and chloride ions present. There are three potential sources of chloride ion:

1. Electrochemical reduction of SOCl₂.
2. Reaction between CoTnPc species and SOCl₂, and
3. Hydrolysis of thionyl chloride producing HCl.

Case 3 was eliminated by using anhydrous conditions and bubbling nitrogen through the SOCl₂ prior to use to displace the HCl already present. In all of our studies, electronic spectroscopy showed that less than 5% of the CoTnPc was protonated due to the HCl from the thionyl chloride.

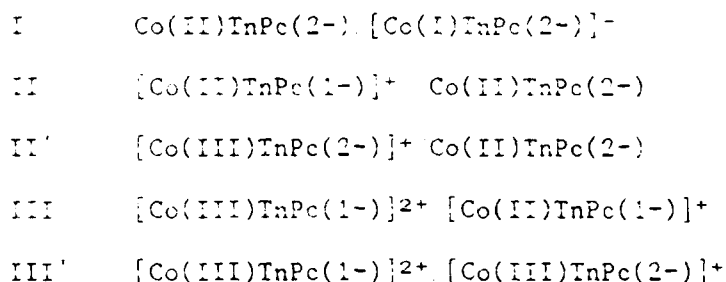
Before the addition of thionyl chloride to Co(II)TnPc(2-) in DCB the [Co(II)TnPc(1-)]⁺/Co(II)TnPc(2-) redox couple (II) yielded a double wave. Co(II)TnPc species are known to aggregate³⁴ and such aggregation can cause splitting of waves in the cyclic voltammogram.³⁵ After adding SOCl₂,

however, this couple yielded a single wave. The effect of SOCl_2 on the Co(II)TnPc(2-) redox couple can be explained in terms of the formation of a $(\text{SOCl}_2)\text{Co(II)TnPc(2-)}$ adduct that was observed above using electronic spectroscopy. Axial coordination of SOCl_2 to Co(II)TnPc will greatly reduce aggregation and hence the first oxidation couple yields a single wave. It is also possible that chloride ions could be responsible for the collapse of the double wave. Electronic spectroscopy, however, has shown that SOCl_2 binds much more strongly to Co(II)TnPc(2-) than Cl^- . A thousand times excess of chloride ions are needed to obtain a limiting spectrum of $[\text{ClCo(II)TnPc(2-)}]^-$ whereas Co(II)TnPc(2-) is completely converted to $(\text{SOCl}_2)\text{Co(II)TnPc(2-)}$ after the addition of one equivalent of SOCl_2 .

$[\text{Co(I)TnPc(2-)}]^-$ is not expected to bind axial ligands because of the lower oxidation state of the cobalt and the d^8 , square planar configuration of the molecule. The shift of the $\text{Co(II)TnPc(2-)} / [\text{Co(I)TnPc(2-)}]^-$ couple (I) in the presence of SOCl_2 (Table 3), therefore, reflects the preferential binding of SOCl_2 to Co(II)TnPc(2-) over $[\text{Co(I)TnPc(2-)}]^-$. If the thionyl chloride is donating electron density to the Co(II) metal center, $(\text{SOCl}_2)\text{Co(II)TnPc(2-)}$ will be more difficult to reduce than free Co(II)TnPc(2-) and the half wave potential of the $\text{Co(II)}/\text{Co(I)}$ wave will shift in the negative direction (as observed) due to the removal of Co(II)TnPc(2-) as the thionyl chloride adduct.

The first oxidation couple of CoTnPc in the presence of SOCl_2 is more difficult to assign because oxidation could occur either at the Co(II) metal center or at the Pc(2-) ligand. Two different oxidized species are possible, $[\text{Co(II)TnPc(1-)}]^+$ or $[\text{Co(III)TnPc(2-)}]^+$, depending on the nature of the solvent and electrolyte present. Previous work²³ has shown that Co(II)TnPc(2-) is oxidized to $[\text{Co(II)TnPc(1-)}]^+$ in DCB/TBAP and

to $[\text{Co(III)TnPc(2-)}]^+$ in DMF TBAP. In DMF solution, coordination of the solvent to the Co center favors the formation of the Co(III) species. The different redox couples of CoTnPc have been defined as follows:



As can be seen in Table 3, the half-wave potentials for couples II and II' only differ by 50 mV, making it difficult to determine the chemistry involved from the potential alone.

The oxidation potentials of CoTnPc in the presence of chloride ion (TBACl) are identical, within experimental error, to those in the presence of 28 equivalents of thionyl chloride. This suggests that the redox processes are the same for both systems. In the presence of TBACl it was shown by spectroelectrochemistry (Table 1,i) that oxidation of Co(II)TnPc(2-) by one electron yields $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$. Hence, in DCB/TBACl and DCB/SOCl₂ the first oxidation couple is $[\text{Co(III)TnPc(2-)}]^+ / \text{Co(II)TnPc(2-)}$ (couple II' in Table 3).

Chloride ions are needed over SOCl₂ for the production of $[\text{Co(III)TnPc(2-)}]^+$ because reaction 2 does not proceed in the presence of excess SOCl₂, but only proceeds in the presence of additional chloride ions. Cyclic voltammetry has also shown that Co(III)TnPc species preferentially bind Cl⁻ over SOCl₂. When CoTnPc is added to an electrochemical cell containing SOCl₂ ($[\text{SOCl}_2] = 2.8 \times 10^{-3}\text{M}$ and $[\text{CoTnPc}] = 2.2 \times 10^{-4}\text{M}$) the current

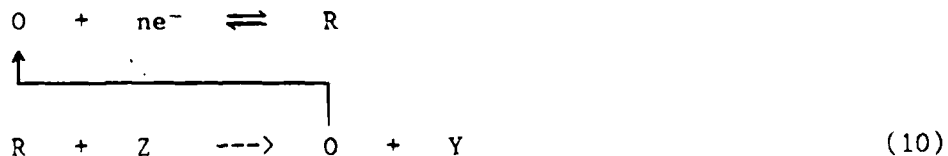
associated with the $\text{Cl}_2/2\text{Cl}^-$ couple is dramatically reduced (the anodic current due to $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$ was $1.16 \mu\text{A}$ before the addition of CoTnPc and $0.26 \mu\text{A}$ afterwards using a Pt disk electrode of area $1.02 \times 10^{-3} \text{ cm}^2$). The chloride ions result from the reduction of SOCl_2 and since $[\text{ClCo(II)TnPc(2-)}]^-$ is oxidized to $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ before chloride ions are oxidized to chlorine gas, one chloride ion is lost at the electrode surface for every $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ produced.

In summary, we propose the following redox couples for the cyclic voltammetry of CoTnPc in the presence of SOCl_2 .

- I $(\text{SOCl}_2)\text{Co(II)TnPc(2-)} / [\text{Co(I)TnPc(2-)}]^-$
- II' $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^- / (\text{SOCl}_2)\text{Co(II)TnPc(2-)}$
- III' $\text{Cl}_2\text{Co(III)TnPc(1-)} / [\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$

The identity of the waves could be further complicated, however, depending upon the kinetics of the equilibria reactions involved.

With an excess of SOCl_2 present, the various CoTnPc species, produced at the electrode surface, in lower oxidation states than $\text{Cl}_2\text{Co(III)TnPc(1-)}$ can be reoxidized by the thionyl chloride in solution. This is an example of a catalytic EC' mechanism:³⁶



O represents $[\text{Co(III)TnPc(1-)}]^{2+}$, Z is SOCl_2 , Y represents the SOCl_2 reduction products and R is either $[\text{Co(I)TnPc(2-)}]^-$, Co(II)TnPc(2-) or $[\text{Co(III)TnPc(2-)}]^+$. An important feature in the differential-pulse voltammogram of CoTnPc is that the current ratio (i_a/i_c) for the

$\text{Co(II)TnPc(2-)} / [\text{Co(I)TnPc(2-)}]^-$ redox couple changed from unity to 0.91 in the presence of 1.5 equivalents of thionyl chloride. The cathodic current is larger than the anodic current because of the oxidation of $[\text{Co(I)TnPc(2-)}]^-$ by SOCl_2 . Reaction 5 will increase i_c due to reduction of the $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ produced, and decrease i_a due to removal of $[\text{Co(I)TnPc(2-)}]^-$. There is, in effect, a catalytic current due to the conversion of the reduced species to an oxidized species by the SOCl_2 . This was only observed for the redox couple involving $[\text{Co(I)TnPc(2-)}]^-$. While $[\text{Co(I)TnPc(2-)}]^-$ reacts rapidly with thionyl chloride catalytic currents were not observed for the other CoTnPc redox couples because the reaction of SOCl_2 with Co(II)TnPc(2-) and $[\text{Co(III)TnPc(2-)}]^+$ was too slow to be observed on the time scale of the DPV experiment (5mV/s).

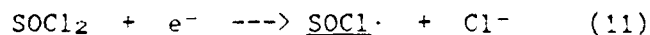
Lithium cell: Rest Potential Measurements.— The addition of AlCl_3 to a $\text{Li/SOCl}_2/\text{C}$ cell had a large effect (0.63V shift) on the Li^+/Li redox couple; it became much more favorable to produce Li^+ . This was reflected in an increase of the cell potential by the same amount (0.64V). Hence, the AlCl_3 must be stabilizing the LiCl product as the LiAlCl_4 complex salt.

Theoretical calculations³⁷ predict a change in potential between 530 and 630 mV, depending upon the value of the equilibrium constant for the reaction.

Previous work by Madou et al.^{38,39} indicated that the potential of the lithium electrode is not affected by AlCl_3 . They added AlCl_3 to a cell already containing LiAlCl_4 electrolyte. Since LiAlCl_4 can dissociate to LiCl and AlCl_3 , their experiment was not as sensitive to the addition of AlCl_3 as the one performed above in which AlCl_3 was added to neat SOCl_2 .

Rest potential measurements of the carbon cathode in a $\text{Li/SOCl}_2/\text{C}$ cell revealed that thionyl chloride is a strong oxidizing agent ($E=0.58$ to 0.79V

vs SCE in Table 4). This is not obvious, however, from the cyclic voltammogram of SOCl_2 where the reduction wave of SOCl_2 peaks at -0.69V vs AgCl/Ag . A large overpotential must, therefore, be required to overcome the activation energy barrier of adding an electron to SOCl_2 . This implies the formation of a high energy intermediate, for example,

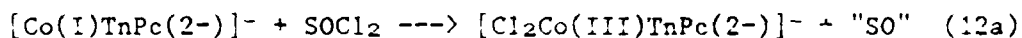


A very recent paper⁷ reports evidence that the first charge transfer step is rate determining. The formation of a high energy intermediate could explain the two-electron reactions observed between CoTnPc and SOCl_2 . The $\text{SOCl}\cdot$ intermediate, formed after the transfer of one electron from CoTnPc to SOCl_2 (perhaps bound to the cobalt center), may drive the transfer of a second electron to produce SO and Cl^- in some kind of concerted reaction.

The addition of Co(II)TnPc(2-) (oxidized to $\text{Cl}_2\text{Co(III)TnPc(1-)}$ by SOCl_2) to the thionyl chloride cells described in Table 4 had little effect on the lithium, thionyl chloride and overall cell potentials. Madou and coworkers^{38,39} have also studied the effect of CoPc in a Li/SOCl_2 cell. Addition of CoPc increased the rest potential of the cell, but only by 100 mV. Because the changes in electrochemical potentials are small, one could infer that the thermodynamics of the reaction between SOCl_2 and Li are unchanged in the presence of CoPc , i.e., the products of the reaction are the same. This, however, would be premature since the concentration of CoPc dissolved in the thionyl chloride is very small, many orders of magnitude less than the amount of SOCl_2 .

Implications for Li/SOCl₂ Batteries.— If the carbon cathode of a Li/SOCl₂ battery is coated or impregnated with cobalt phthalocyanine the thionyl chloride will oxidize the exposed CoTnPc to Cl₂Co(III)TnPc(1-) under open circuit conditions. In closed circuit, however, the carbon cathode will reduce the oxidized cobalt phthalocyanine. To determine the lowest oxidation state of CoTnPc in a Li/SOCl₂/C battery the electronic spectrum of Co(II)TnPc(2-) in DCB was monitored in the presence of a piece of graphite inserted into a lump of lithium (see expt. section). The Co(II)TnPc(2-) was reduced to [Co(I)TnPc(2-)]⁻ (Table 1,d). The [Co(I)TnPc(2-)]⁻ solution was allowed to stand in contact with the Li/C for two days to ensure that this was indeed the lowest oxidation state of CoTnPc achievable under these conditions.

The following mechanism is, therefore, evident for the reduction of thionyl chloride in a Li/SOCl₂/(CoTnPc,C) battery.



summing to:



The CoTnPc will act as a mediator between the carbon cathode and the thionyl chloride. Assuming good electrical contact between the cobalt phthalocyanine catalyst and the carbon cathode, the oxidation state of the

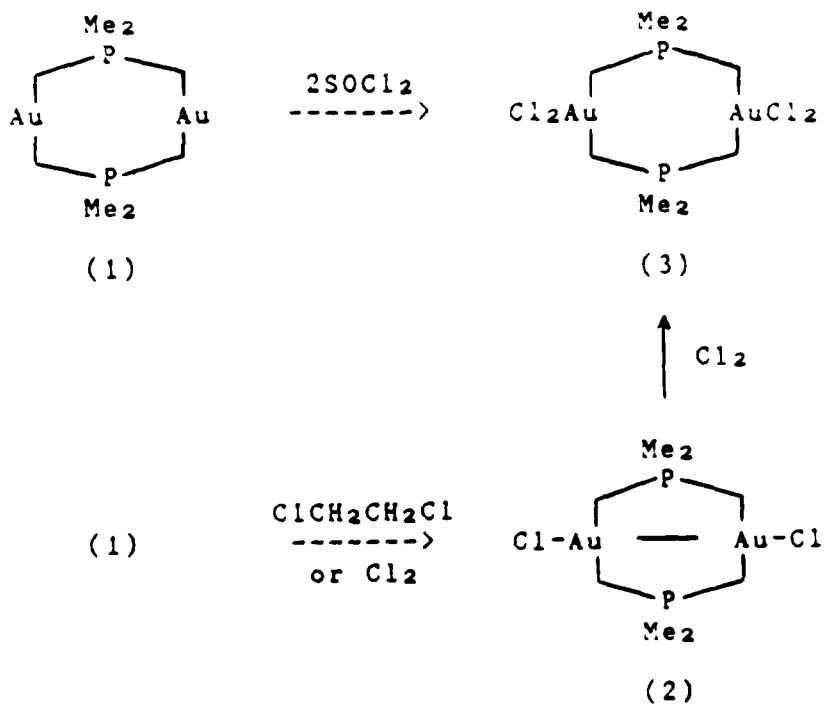
CoTnPc will fluctuate, from $[\text{Co(I)TnPc(2-)}]^-$ (reduced by the cathode) to $\text{Cl}_2\text{Co(III)TnPc(2-)}$ (oxidized by SOCl_2). As a result, the SOCl_2 will be catalytically reduced by two electrons. "SO" and chloride ions may not be the actual products of the thionyl chloride reduction. These species have been chosen only because they are the simplest two-electron reduction products of SOCl_2 . Riga⁴⁰ however, does report that sulphur and chloride ions are products of thionyl chloride reduction by iron and molybdenum phthalocyanines. The sulphur probably results from the disproportionation reaction of SO to yield S and SO_2 . Some evidence for the existence of SO has been recently reported.⁷

A two-electron reduction process could result in a safer Li/ SOCl_2 battery by eliminating reactive intermediates that may form when SOCl_2 is reduced at a bare carbon cathode. The mechanism for the reduction of SOCl_2 at a carbon electrode is not well understood. The generally accepted cell reaction is the two-electron reduction of thionyl chloride to sulphur, sulphur dioxide and chloride ion. Many other species, however, have been identified.^{1,3-6} Doddapaneni¹³⁻¹⁵ proposes that the first step is the reduction of SOCl_2 to the $\text{SOCl}\cdot$ radical (Equation 11). The $\text{SOCl}\cdot$ radical dimerizes and then decomposes to several intermediate species, some of which are known to cause safety hazards. When metal phthalocyanines are present, Doddapaneni proposes that the $\text{SOCl}\cdot$ radical (adsorbed on the MPc) can undergo a further one-electron reduction. Our work has shown this to be the case.

SOCl_2 as a Two-electron Oxidizing Agent.-Thionyl chloride has been shown to oxidize CoTnPc by two electrons. Whether the reaction represents a true two-electron transfer or two step-wise, but concerted, one-electron transfers remains to be solved. Schmidbaur and Jandik⁴¹ have also reported

a two-electron oxidation using thionyl chloride. The gold(I)dimethylphosphonium-bis-methylide dimer **1** is oxidized to the gold(III) complex **3**, without any gold(II) intermediate being observed. Using 1,2-dichloro or 1,2-dibromo-ethane, on the other hand, the gold(I) dimer is converted into the Au-Au bonded gold(II) complex. Ethylene is eliminated in this oxidative addition process. Compound **2** can also be prepared using chlorine or bromine. Excess halogen will convert either **1** or **2** into the Au(III) complex **3**.

The two-electron reaction between thionyl chloride and the gold(I)dimethylphosphonium-bis-methylide dimer parallels our observed reactions between CoTpPc species and SOCl_2 . The similarity between these two systems is remarkable; two-electron oxidations are observed with no sign of the one-electron intermediate being formed, and, in each case, the one-electron oxidation product is stable and can be prepared using alternative methods.



The kinetics of the reaction between CoTnPc and SOCl_2 are presently being studied to obtain more mechanistic information.⁴²

Conclusions

1. Thionyl chloride reacts with $[\text{Co(I)TnPc(2-)}]^-$ and Co(II)TnPc(2-) to give two-electron oxidized species (Equations 5 and 6). $[\text{Co(III)TnPc(2-)}]^+$ is oxidized by one electron to $[\text{Co(III)TnPc(1-)}]^{2+}$. Co(II)TnPc(2-) first forms a mono thionyl chloride adduct and is then oxidized to $\text{Cl}_2\text{Co(III)TnPc(1-)}$.
2. A comproportionation reaction is observed between $[\text{Co(I)TnPc(2-)}]^-$ and its two-electron oxidized product $[\text{Cl}_2\text{Co(III)TnPc(2-)}]^-$ (Equation 1).
3. The lowest possible oxidation state of CoTnPc in a $\text{Li/SOCl}_2/\text{C}$ battery is $[\text{Co(I)TnPc(2-)}]^-$ due to reduction at the carbon cathode.
4. A two-electron catalytic cycle is indicated for the reduction of thionyl chloride in a $\text{Li/SOCl}_2/(\text{CoTnPc,C})$ battery. A two-electron reduction process could result in a safer Li/SOCl_2 battery by eliminating reactive intermediates that may form when SOCl_2 is reduced by one electron at a carbon cathode not treated with cobalt phthalocyanine.

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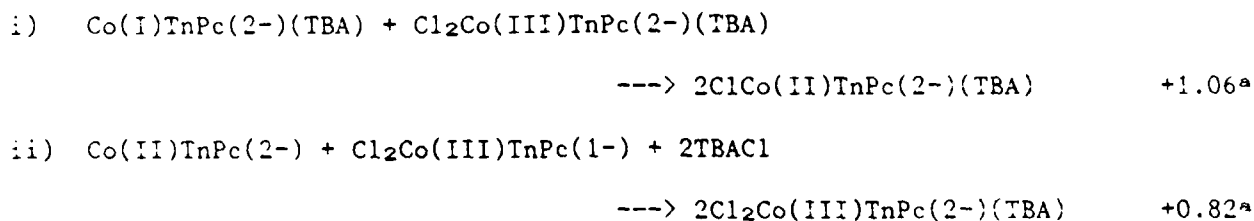
Table 1. Electronic absorption maxima of cobalt tetraneopentoxypthalocyanines.

Species ^a	Footnote	λ nm ($\epsilon, M^{-1}cm^{-1}$)			
[Co(I)TnPc(2-)]-[TBA] ⁺	b	356sh	472(38100)	645(16800)	710(54700)
	c	313(57900)	350sh	471(33300)	643(18400) 708(45000)
[Co(I)TnPc(2-)]-[Li/TBA] ⁺	d	359sh	471(36600)	647(17200)	709(51300)
Co(II)TnPc(2-)			383(13800)	614(24200)	680(83800)
	e	330(40700)	380(13800)	612(25700)	678(72400)
[ClCo(II)TnPc(2-)]-[TBA] ⁺	f	347		603(27400)	669(85000)
(SOCl ₂)Co(II)TnPc(2-)	g	343	393(25900)	623(32000)	686(93900)
[Cl ₂ Co(III)TnPc(2-)]-[TBA] ⁺	h		367(33500)	608(31200)	678(133000)
	i		369(30900)	607(31800)	677(134000)
[(DMF) ₂ Co(III)TnPc(2-)]+[ClO ₄] ⁻	j		355(63100)	610(37200)	676(148000)
Cl ₂ Co(III)TnPc(1-)	k	399(24800)	540(26500)	679(17100)sh	755(20600)br
	l	366sh	404(23000)	540(20600)	680(16700)sh 744(18900)br
(ClO ₄) ₂ Co(III)TnPc(1-)	m	380(23600)	400(24000)	520(16600)	580sh 742(11500)

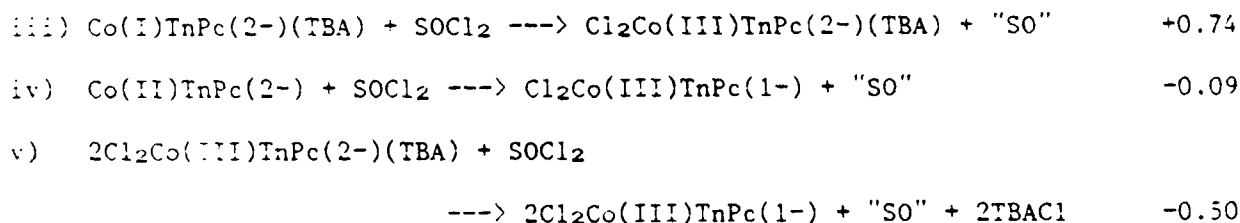
^a[CoTnPc] $\approx 10^{-4}M$ in DCB solution except as otherwise noted. ^bElectrochemical reduction of Co(II)TnPc(2-), [TBAPF₆]=0.048M. ^cElectrochemical reduction of Co(II)TnPc(2-), [TBAP]=0.3M.²³ ^dReduction of Co(II)TnPc(2-) using Li/C with 0.07M TBAPF₆. ^eWith 0.3M TBAP.²³ ^fWith 0.10M TBACl. ^g[SOCl₂]=2.7 X 10⁻³M. ^hFrom the oxidation of Co(I)TnPc(2-) containing 0.07M TBAPF₆ with 4 X 10⁻⁴M SOCl₂. ⁱElectrochemical oxidation of Co(II)TnPc(2-), [TBACl]=0.10M. ^jElectrochemical oxidation of Co(II)TnPc(2-) in DMF solution containing 0.3 M TBAP.²³ ^kFrom the oxidation of Co(II)TnPc(2-) with 0.013M SOCl₂. ^lOxidation of Co(II)TnPc(2-) by chlorine gas. ^mElectrochemical oxidation of Co(II)TnPc(2-), [TBAP]=0.3M.²³ TBAP=tetrabutylammonium perchlorate, DMF=dimethylformamide, br=broad and sh=shoulder.

Table 2. Driving forces (ΔE values) for CoTnPc and SOCl_2 reactions in DCB calculated using the half-wave potentials of CoTnPc in Table 3 and using 0.15V vs Fc^+/Fc (0.64V vs SCE, Table 4) for the reduction potential of SOCl_2 .

CoTnPc Comproportionation Reactions $\Delta E(\text{V})$



CoTnPc + SOCl_2 Reactions^b $\Delta E(\text{V})$



^aThese potential differences are approximately equal to ΔE° .³⁶ Using $\text{RTlnK} = nF\Delta E^\circ$, where $n = 1$ and $T = 294^\circ\text{K}$, yields $K = 1.5 \times 10^{18}$ for (i) and $K = 1.1 \times 10^{14}$ for (ii). ^bFor these calculations it was assumed that SOCl_2 is reduced by two electrons at 0.15V vs Fc^+/Fc in DCB.

Table 3. Electrochemical data for cobalt tetraneopentoxypthalocyanine in DCB.

	$E_{\frac{1}{2}}, V (\Delta E_p, mV)^a$				
	Oxidation				Reduction
	III	III'	II	II'	I
In DCB/TBAP ^b	+0.59 (90)		+0.03 (89)		-0.91 (70)
In DCB/TBAPF ₆ : ^c	+0.69 (63)		+0.17 ^d		-1.01 (104)
			-0.06		
with 6 equiv Cl ⁻ ^e		+0.65 (122)		-0.06 (115)	-1.12
In the presence of SOCl ₂ :					
1.5X free SOCl ₂ ^f		+0.68 (63)		+0.01 (100)	-1.11
28 equiv SOCl ₂ ^g		+0.65 (75)		-0.04 (117)	
In DMF/TBAP ^b		+0.38		-0.02	-0.85 (85)

^aPotentials are reported with respect to the ferrocenium/ferrocene couple. $E_{\frac{1}{2}} = (E_{pa} + E_{pc})/2$ and $E_p = E_{pa} - E_{pc}$. See text for definition of couples. ^bThese literature half-wave potentials and peak separations are for a $1 \times 10^{-4}M$ CoTnPc solution in DCB or DMF containing 0.1M TBAP at a scan rate (ν) of 20mV/s. $i_a = i_c$ and $i_a \approx \nu^{1/2}$. ²³ ^c[CoTnPc] = $1.62 \times 10^{-4}M$ in DCB, [TBAPF₆] = 0.067M. Peak separations were measured by cyclic voltammetry at 100 mV/s. DPV at 5 mV/s was used to determine the half-wave potentials and current ratios. $i_a = i_c$ for the three redox couples. ^dA double wave was observed. The wave at +0.17V was approximately twice as large as the one at -0.06V. ^e[CoTnPc] = $3 \times 10^{-4}M$ in DCB, [TBAPF₆] = 0.07M. [TBACl] = $1.8 \times 10^{-3}M$, ν = 100 mV/s. ^fSame conditions as in (c) except with $2.5 \times 10^{-4}M$ free SOCl₂ (est. from the SOCl₂ reduction current). $i_a = i_c$ for couples II' and III'. $i_a = 0.91 i_c$ for couple I. ^g[CoTnPc] = $1.22 \times 10^{-4}M$, [SOCl₂] = $3.4 \times 10^{-3}M$. [TBAPF₆] = 0.058M in DCB, ν = 50 mV/s. $i_a = i_c$ for couples II' and III'.

Table 4. Open circuit rest potentials in volts of Li/SOCl₂/C cells.

Conditions	E _{cell}	E _{anode} (E _a) vs SCE	E _{cathode} (E _c) vs SCE	E _c -E _a
Using SOCl ₂ : ^a	3.24	-2.57	0.58	3.15
CoTnPc(3 X 10 ⁻⁴ M)	3.25	-2.63	0.58	3.21
1.6M AlCl ₃	3.88	-3.20	0.63	3.83
1.0M AlCl ₃ , 0.6M LiAlCl ₄	3.81	-3.10	0.72	3.82
1.0M AlCl ₃ , 0.6M LiAlCl ₄ , CoTnPc(3 X 10 ⁻⁴ M)	3.81	-3.01	0.72	3.73
Using DCB, 0.07M TBAPF ₆ :				
0.14M SOCl ₂	3.54	-2.87	0.64	3.51
1.4M SOCl ₂	3.72	-2.96	0.74	3.70
3.1M SOCl ₂	3.76	-2.96	0.79	3.75
1.4M SOCl ₂ , CoTnPc(3 X 10 ⁻⁴ M)	3.67	-2.96	0.67	3.63
Literature values in SOCl ₂ : ³⁹				
1.6M LiAlCl ₄	3.6			
1.6M LiAlCl ₄ , CoPc	3.7			
1.6M LiAlCl ₄ , AlCl ₃	3.9			
1.6M LiAlCl ₄ , AlCl ₃ , CoPc	4			
	3.72 (calc for 4Li+2SOCl ₂ →4LiCl+S+SO ₂) ⁴³			

^aThionyl chloride was the only solvent used and was exposed to the air. At room temperature, the maximum solubility of HCl (from the hydrolysis of SOCl₂) is 0.28M.²² The HCl acted as the electrolyte when measuring the electrode potentials in neat SOCl₂.

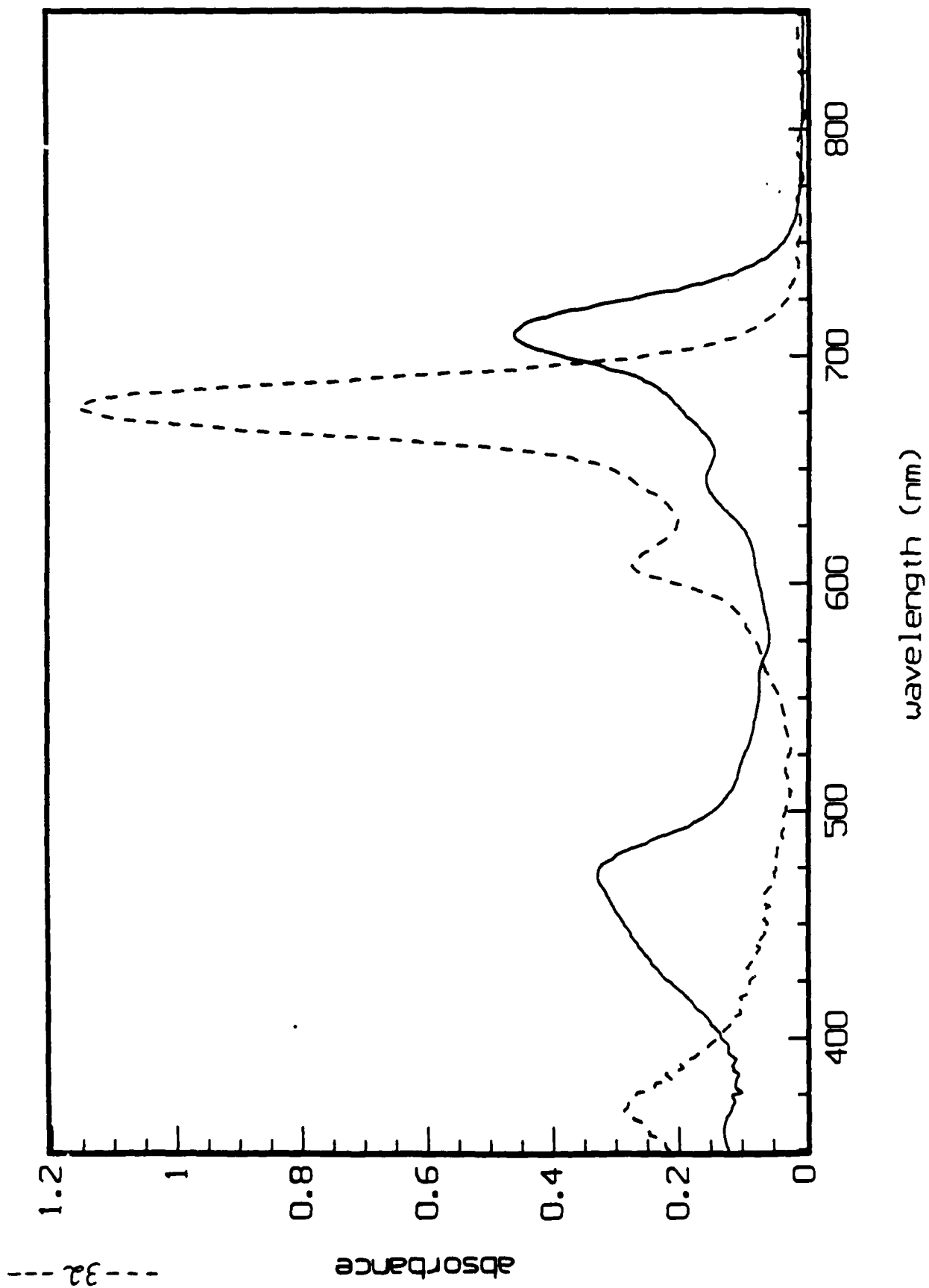
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Figure 1. Electronic absorption spectra of $\text{Co(I)TnPc(2-)}(\text{TBA})$ (—) and its two electron oxidation product $\text{Cl}_2\text{Co(III)TnPc(2-)}(\text{TBA})$ (---) with SOCl_2 in DCB. $[\text{CoTnPc}] = 8.65 \times 10^{-5} \text{ M}$, $[\text{TBAPFe}] = 0.07 \text{ M}$ and $[\text{SOCl}_2] = 4 \times 10^{-4} \text{ M}$.

Figure 2. Electronic absorption spectra of Co(II)TnPc(2-) (—), $(\text{SOCl}_2)\text{Co(II)TnPc(2-)}$ (---) and $[\text{ClCo(II)TnPc(2-)}]^-$ (···) in DCB. $[\text{CoTnPc}] = 6.12 \times 10^{-5} \text{ M}$, $[\text{SOCl}_2] = 2.8 \times 10^{-3} \text{ M}$ for the thionyl chloride adduct, and $[\text{TBACl}] = 0.10 \text{ M}$ for the chloro complex.

Figure 3. Oxidation of Co(II)TnPc(2-) to $\text{Cl}_2\text{Co(III)TnPc(1-)}$ by thionyl chloride in DCB. $[\text{CoTnPc}] = 1.14 \times 10^{-4} \text{ M}$, $[\text{SOCl}_2] = 5.5 \times 10^{-3} \text{ M}$. These spectra were recorded over a period of 11 minutes at room temperature.

Figure 4. Cyclic voltammogram (—, $\nu = 100 \text{ mV/s}$) and DPV (\rightarrow , $\nu = 5 \text{ mV/s}$, 5 mV modulation amplitude) of a DCB solution of CoTnPc and SOCl_2 . $[\text{CoTnPc}] = 1.82 \times 10^{-4} \text{ M}$, $[\text{SOCl}_2] \approx 2.5 \times 10^{-4} \text{ M}$ and $[\text{TBAPFe}] = 0.067 \text{ M}$. The ferrocenium/ferrocene couple occurred at +0.43V vs AgCl/Ag .



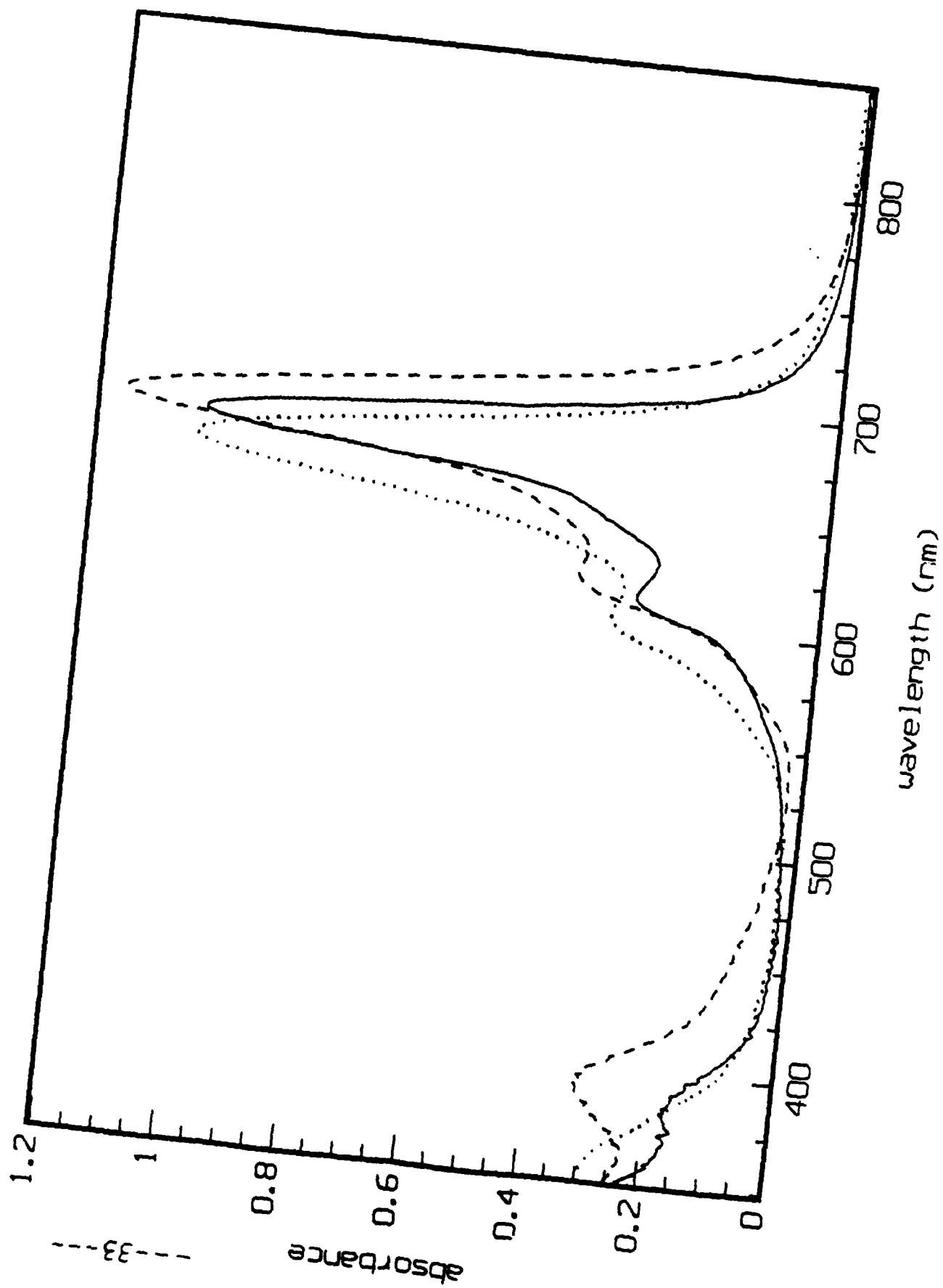


Fig 2

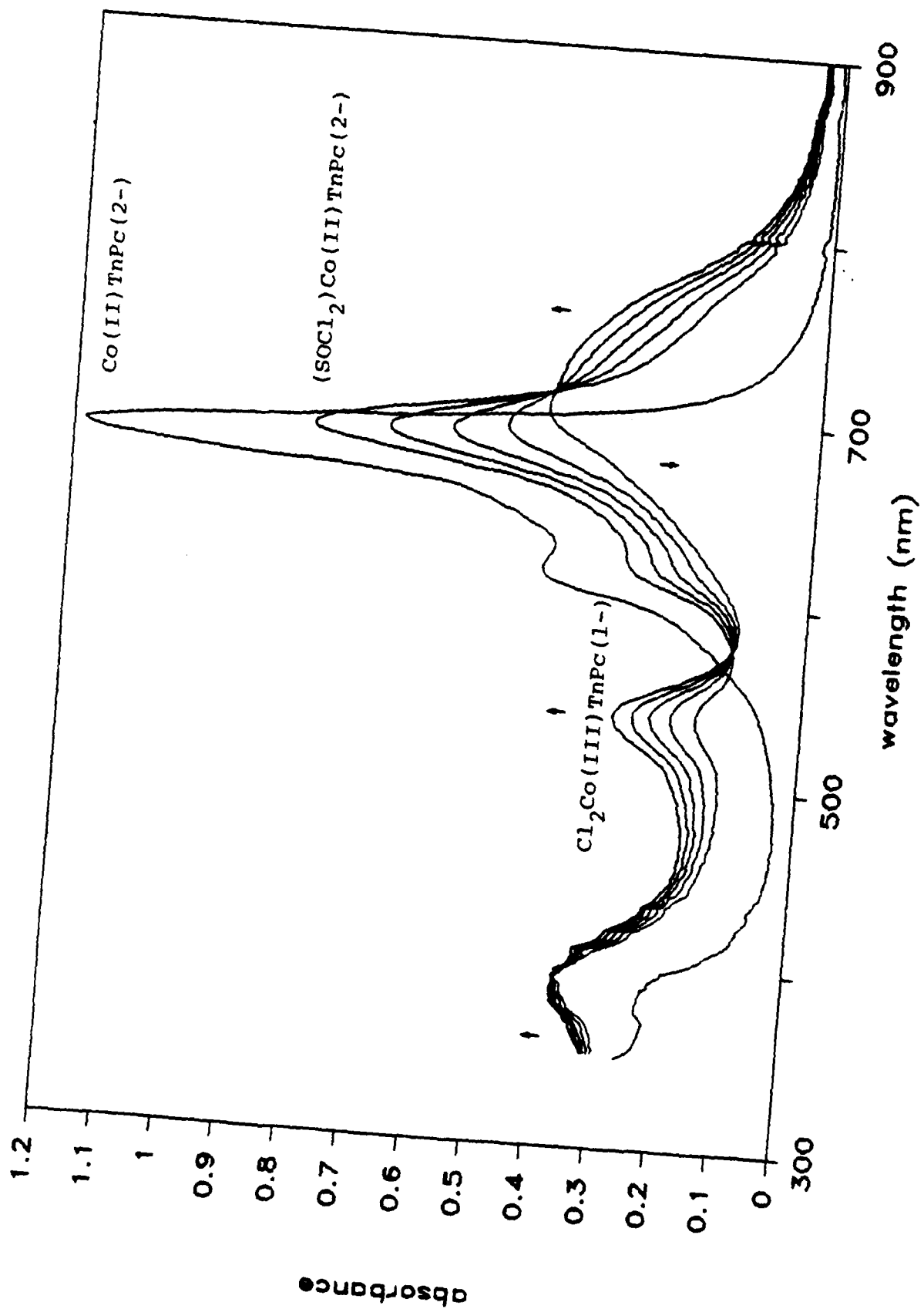


Fig 3

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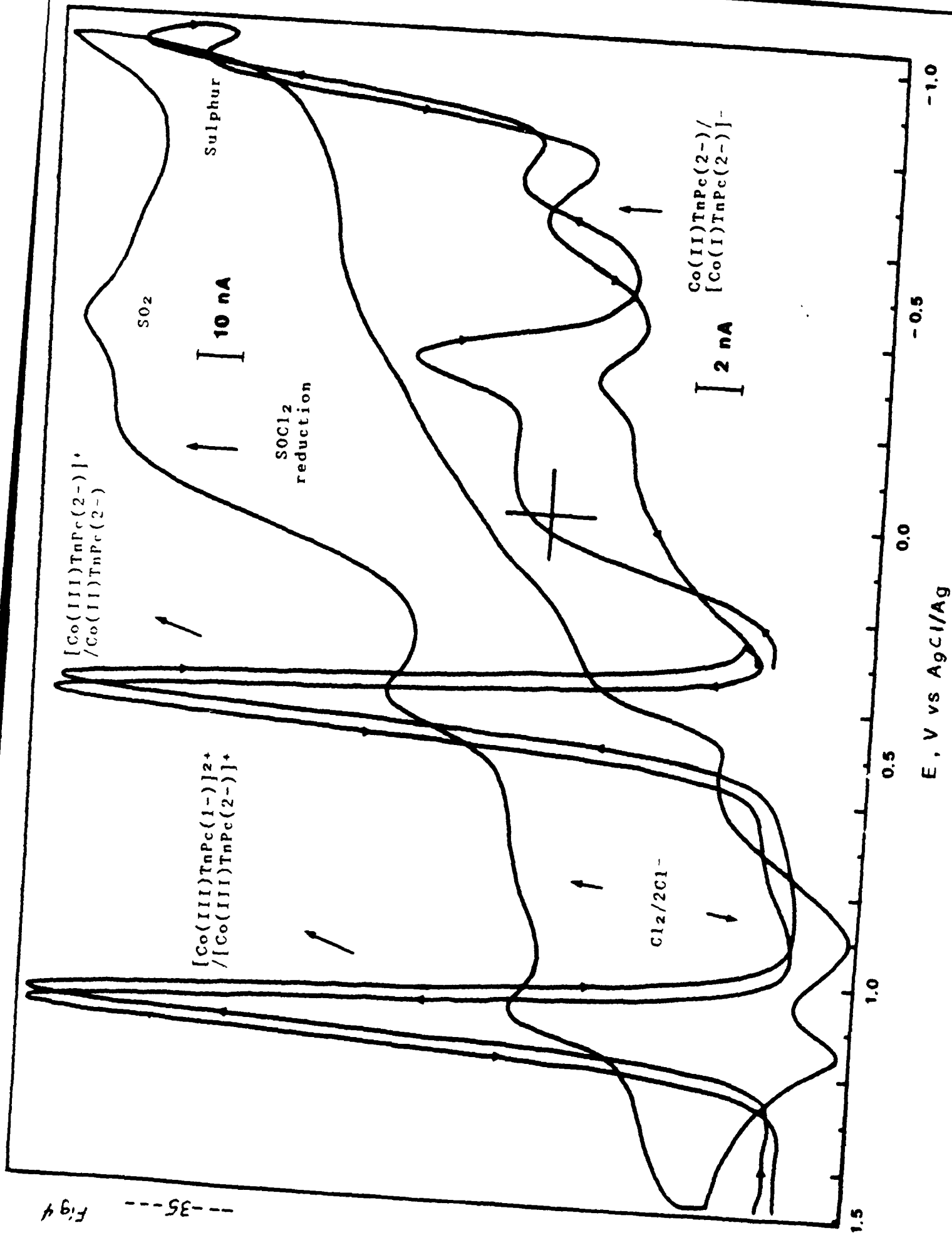


Fig 4 ---35---

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